

Pulse Voltammetry of Chromium at Screen Printed Electrode Modified by Thin Films of Nickel

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ABSTRACT

A rapid and potentially cost-effective electrochemical method is reported for analysis of chromium (VI) using a nickel modified screen printed carbon ink electrode. Electrochemical characteristics of the nickel modified electrode as well differential pulse voltammetric behavior for chromium are discussed. Scanning electron micrographs and elemental analysis of nickel films yield an indication of the structural features of the electrode surface. The nickel electrode detects chromium (VI) over the concentration range of 2-10 ppb. One advantage of this method is that the nickel electrode is sensitive, stable and environmentally friendly compared to mercury film electrodes which are typically used for chromium analysis. The potential development of this method for field analysis is also discussed.

& BACKGROUND INTRODUCTION

Chromium is widely used in industry for a number of diverse products and processes. There are many locations where chromium has been released into the environment primarily into soil and unlined holding ponds. One of the major concerns for potential human exposure is the release, transport beyond waste site boundaries, and contamination of the ground water flow systems. Although many of these waste sites have been characterized and are under remediation, analytical monitoring is often required during and after cleanup. Consequently, rapid, inexpensive and field portable methods for chromium are of considerable value. This metal has been shown to cause toxic and carcinogenic effects in humans and animals. Chromium is found as an environmental contaminant primarily in the valence forms Cr(VI) and Cr(III). In particular, Cr(VI) has been shown to be carcinogenic and extremely toxic. Once inside cells, Cr(VI) is reduced through reactive chromium intermediates such as Cr(V) and Cr(IV) to the ultimate kinetically stable Cr(III) by cellular reductants. Therefore, intermediate oxidation states probably play an important role in Cr(VI)-induced toxicity. Electrochemical methods are frequently used for direct determination of chromium using mercury and chemically modified electrodes. Although mercury is well established as an electrode material, it is itself hazardous and consequently generates concerns for health and safety. Electrochemical deposition techniques are well known for modification of various electrode surfaces for the analysis of trace metals. Variables, such as current density and applied potential, allow for a great deal of control over this process. Optimization of these parameters can result in deposits having desirable electrode properties. We report an electrodeposition technique to modify screen printed carbon surfaces with nickel to form an inexpensive disposable alternative to mercury electrodes for measurement of Cr(VI). In addition, microstructure of electrode surface modified by nickel is also examined to evaluate the chemical composition as well as structural characteristics of the modified electrode surface. The nickel modified screen printed carbon electrode is stable, sensitive and environmentally friendly.

& SUMMARY CONCLUSIONS

These results indicate that the herein described nickel film modified screen printed carbon ink electrode is well suited for the determination of Cr(VI) in solution. These electrodes are:

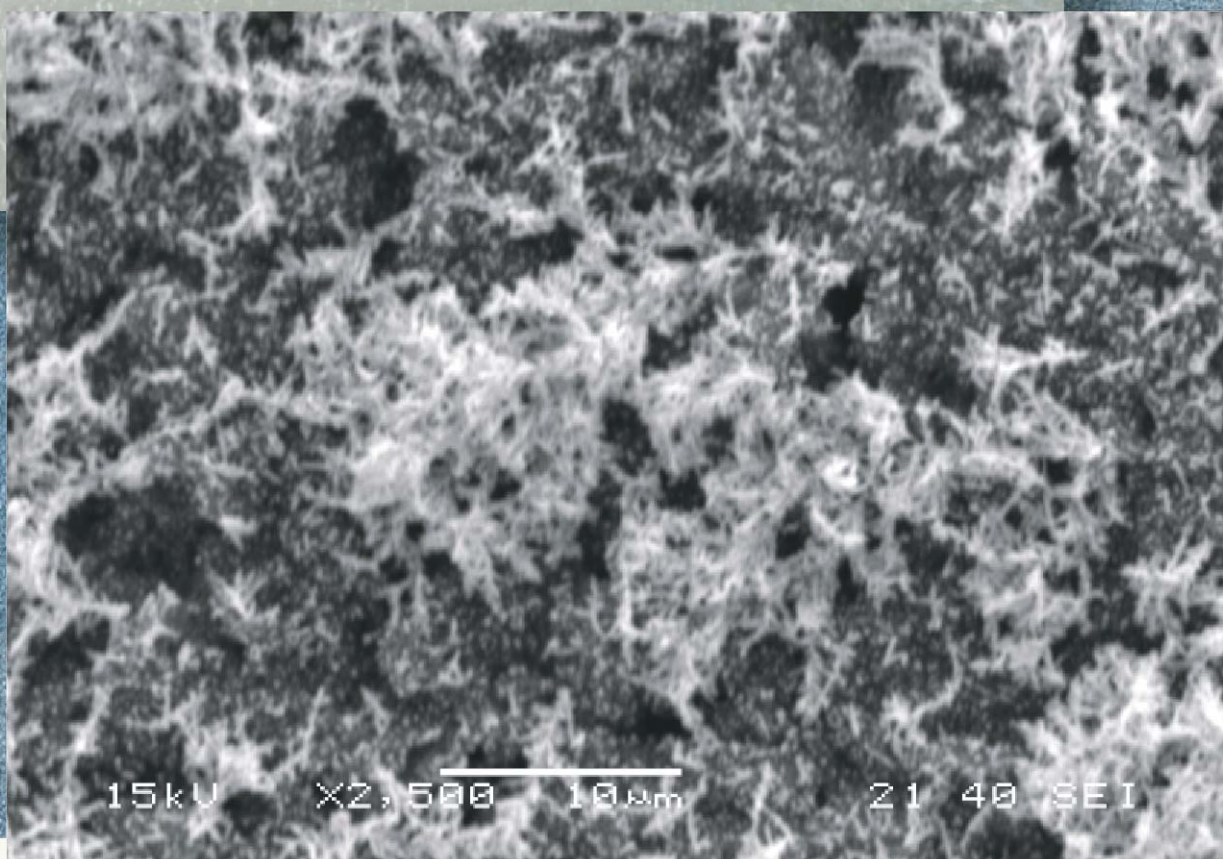
- ✦ Inexpensive (about \$1 each)
- ✦ Disposable
- ✦ Sensitive (2 ppb for Cr(VI))
- ✦ Environmentally Friendly (mercury free)

Given the additional complexity and toxicity issues associated with handling mercury electrodes in a potential field monitoring setting, the nickel film electrode appears to be a good candidate for further development for a voltammetry-based assay for toxic metal ions such as Cr(VI).

METHODS

Electrochemical measurements were made using a BAS 100 electrochemical analyzer. The electrolyte solution for electrodeposition was as follows: 5 mL of 1mM NiCl₂, 2 mL of 0.01M NaOH, 1 mL of 10-15% HCHO, and 2 mL 10% of 0.1M sodium acetate. Electrodeposition was run over a potential range of -0.1V to -0.3V for 5 to 10 minutes. The concentrations of HCHO and sodium acetate were the most dominant factors in determining the growth of the nickel film. The coating density appeared to increase with the concentration of HCHO up to between 10 and 15%. The presence of NaOH also increased the deposition rate. After deposition, the electrode was dried in air and characterized by scanning electron microscopy as well as elemental analysis. The differential pulse voltammetric analysis of Cr(VI) (2-10 ppb) was carried out in 10 mL cell with PBS buffer at scan rate of 100 mV/sec.

The electrode strips were 1mm x 2.5cm printed on ceramic substrate (1cm x 3cm). The electrode consisted of silver ink for the reference/counter electrode and carbon ink for the working electrode. Dielectric separated the leads from the working portion of the electrode.



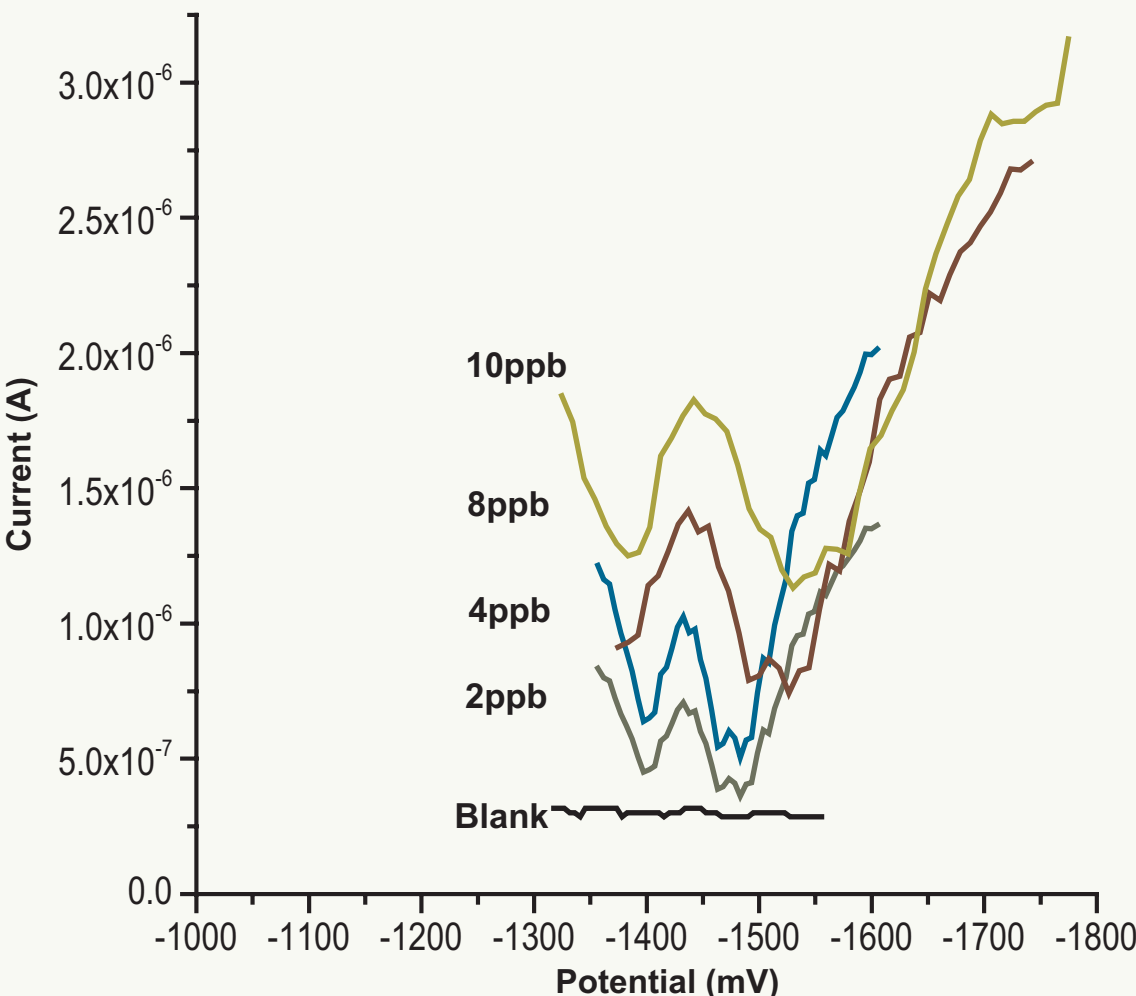
The microstructure of the nickel deposited film on screen printed carbon electrode in transverse section is shown in this scanning electron micrograph. The coating appears to be uniform and is representative of numerous sections observed for several electrodes.

NOTICE

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), funded this research and approved its presentation. The actual presentation has not been peer reviewed by EPA. Nirankar Mishra gratefully acknowledges the National Research Council Fellowship Program.

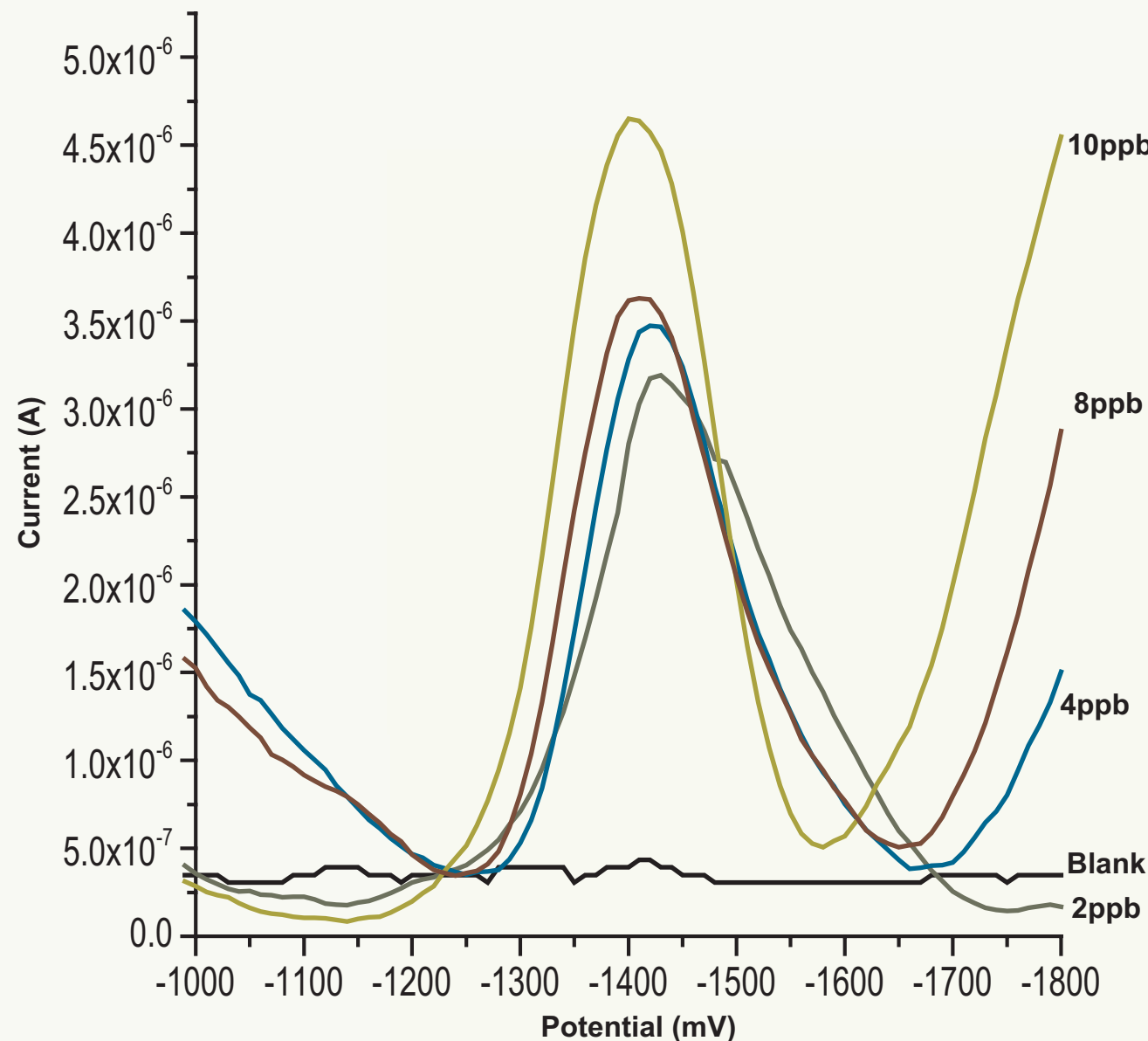
RESULTS

Differential pulse voltammograms of Cr(VI) using a hanging mercury drop electrode yielded a well defined peak at around -1.45V in larger trough. The samples were stirred and oxygen was not removed from the buffer.

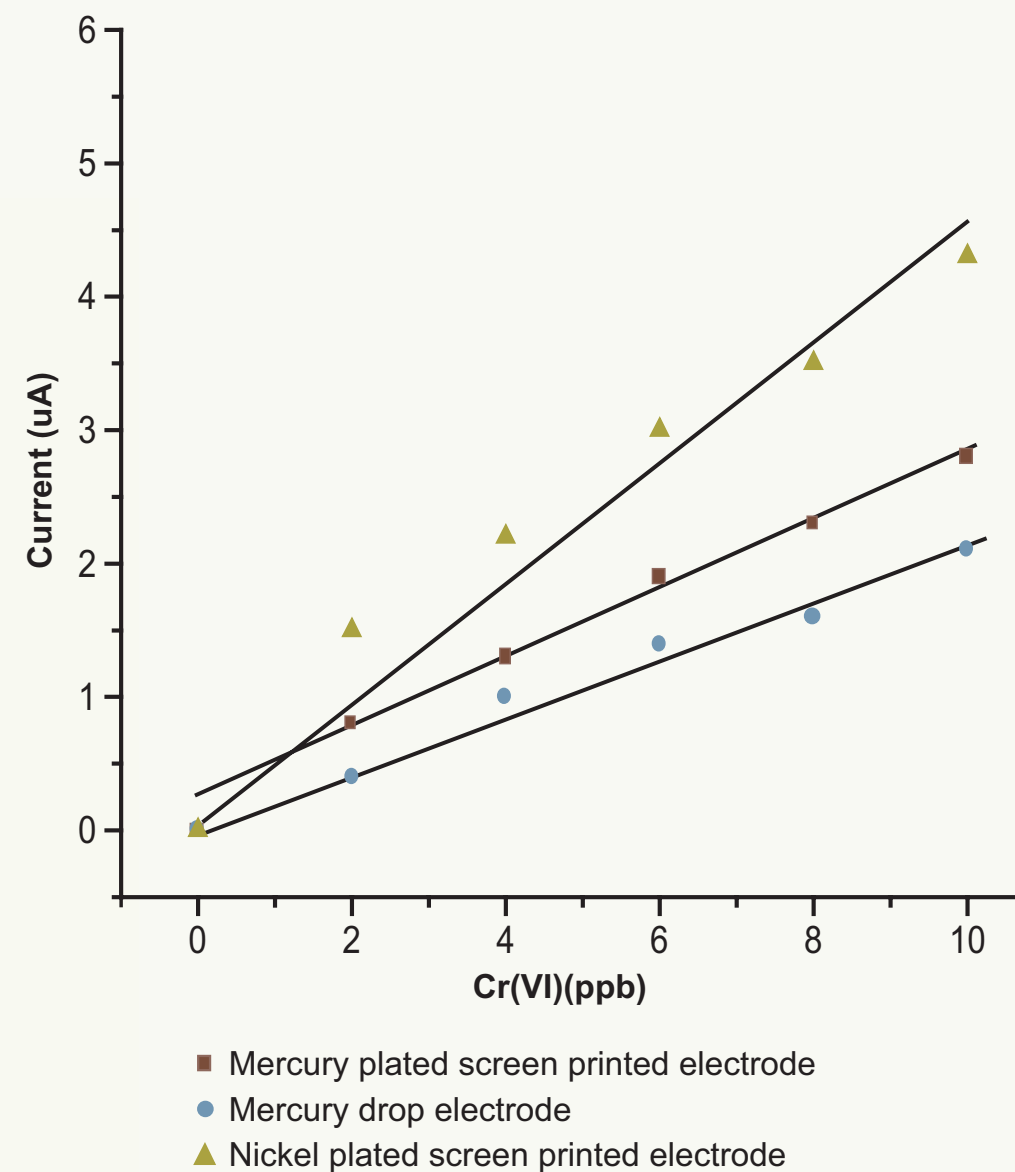


Differential pulse voltammogram Cr(VI) at hanging mercury drop electrode

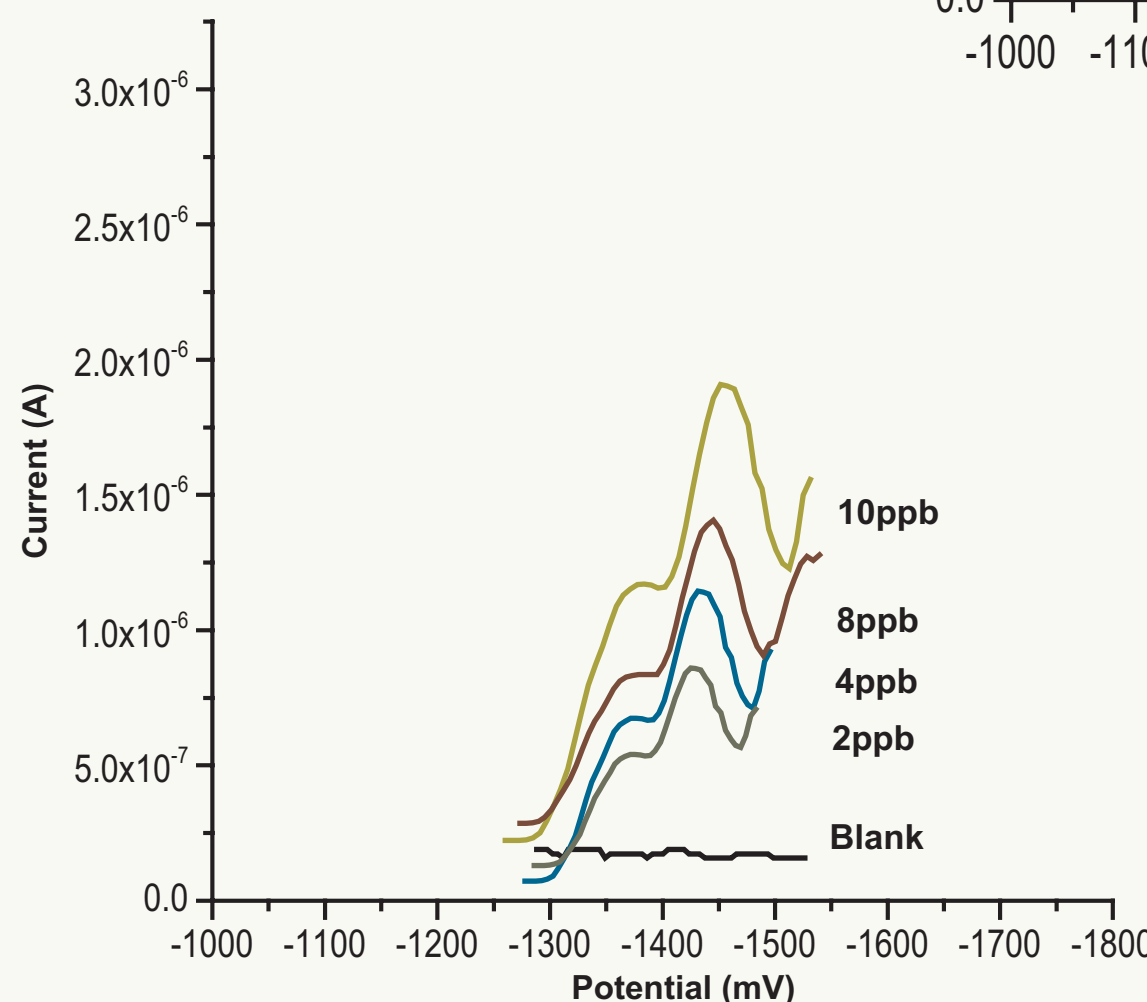
The nickel modified screen printed electrode yielded the best defined signal with a peak around -1.40V. The current for nickel modified electrode was about three times of the mercury modified screen printed electrode.



The increased sensitivity of the nickel modified electrode is reflected as an increased response slope over both the mercury and mercury modified screen printed electrode.



The comparatively better defined peak at around -1.43V was obtained for Cr(VI) at mercury modified screen printed carbon ink electrode than for the hanging mercury drop.



Differential pulse voltammogram Cr(VI) at mercury modified screen printed carbon electrode

Interferences in the Determination of Cr(VI) at Nickel Modified Screen Printed Carbon Electrode

SALT/IONS	COMMENT
1. Acetate, citrate, nitrate, thiosulphate, nitrite, sulphate	No apparent interference at concentrations less than 5%
2. Fe(III), Cd(II), Cu(II), Pb(II), Zn(II), Cr(III), Ga(III)	No apparent interference at concentrations up to 10 times that of Cr(VI)
3. Pd(II), Mn(II)	Begins to show interference at concentrations above 10 times that of Cr(VI)

Interferences with the detection of Cr(VI) were noted with Pd(II) and Mn(II) at concentrations above 10 times of Cr(VI). Ions such as Cr(III), Fe(III), Cd(II), Pb(II), Zn(II) and Ga(III) showed no interference with measurement of Cr(VI) even at concentrations 10 times that of the target ion.